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(54) Title: PROCESS FOR THE CONTINUOUS GAS-PHASE (CO-)POLYMERISATION OF OLEFINS IN A FLUIDISED BED REACTOR

(57) Abstract: The present invention relates to a process for the continuous gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst characterised in that the polymerisation is performed in the presence of a process aid additive.

PROCESS FOR THE CONTINUOUS GAS-PHASE
(CO-)POLYMERISATION OF OLEFINS IN A FLUIDISED BED REACTOR

The present invention relates to a process for the continuous gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst.

The present invention also relates to a process for preventing fouling during the
5 continuous gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst.

Processes for the co-polymerisation of olefins in the gas phase are well known in the art. Such processes can be conducted for example by introducing the gaseous monomer and comonomer into a stirred and/or gas fluidised bed comprising polyolefin
10 and a catalyst for polymerisation.

In the gas fluidised bed polymerisation of olefins, the polymerisation is conducted in a fluidised bed reactor wherein a bed of polymer particles is maintained in a fluidised state by means of an ascending gas stream comprising the gaseous reaction monomer. The start-up of such a polymerisation generally employs a bed of polymer particles
15 similar to the polymer which it is desired to manufacture. During the course of polymerisation, fresh polymer is generated by the catalytic polymerisation of the monomer, and polymer product is withdrawn to maintain the bed at more or less constant volume. An industrially favoured process employs a fluidisation grid to distribute the fluidising gas to the bed, and to act as a support for the bed when the
20 supply of gas is cut off. The polymer produced is generally withdrawn from the reactor via a discharge conduit arranged in the lower portion of the reactor, near the fluidisation grid. The fluidised bed consists in a bed of growing polymer particles. This bed is

maintained in a fluidised condition by the continuous upward flow from the base of the reactor of a fluidising gas.

The polymerisation of olefins is an exothermic reaction and it is therefore necessary to provide means to cool the bed to remove the heat of polymerisation. In the
5 absence of such cooling the bed would increase in temperature and, for example, the catalyst would become inactive or the bed would begin to melt. In the fluidised bed polymerisation of olefins, the preferred method for removing the heat of polymerisation is by supplying to the polymerisation reactor a gas, the fluidising gas, which is at a temperature lower than the desired polymerisation temperature, passing the gas through
10 the fluidised bed to conduct away the heat of polymerisation, removing the gas from the reactor and cooling it by passage through an external heat exchanger, and recycling it to the bed. The temperature of the recycle gas can be adjusted in the heat exchanger to maintain the fluidised bed at the desired polymerisation temperature. In this method of polymerising alpha olefins, the recycle gas generally comprises the monomer and
15 comonomer olefins, optionally together with, for example, an inert diluent gas such as nitrogen or a gaseous chain transfer agent such as hydrogen. Thus, the recycle gas is used to supply the monomer to the bed, to fluidise the bed, and to maintain the bed at the desired temperature. Monomers consumed by the polymerisation reaction are normally replaced by adding make up gas or liquid to the polymerisation zone or reaction
20 loop.

It is well known that Ziegler-Natta type catalysts can advantageously be used for the (co-)polymerisation of olefins, particularly in slurry processes as well as in gas phase processes. It is also reported in the literature that these catalysts are prone to fouling problems in olefin gas phase polymerisation processes.

25 While the man in the art specialised in olefin gas phase polymerisation has made a lot of progresses in the understanding of the fouling phenomena associated with the use of Ziegler-Natta catalysts, there is still a need in the art to find a process for producing more successfully polyolefins on gas phase industrial plants using such a Ziegler-Natta type catalyst.

30 The Applicants have now unexpectedly found a simple and efficient process which allows us to improve the gas phase polymerisation of olefins using a Ziegler-Natta type catalyst. This was done through a detailed analysis of the rare problems occurring

during the olefin gas phase polymerisation using a Ziegler-Natta type catalyst. Amongst those problems, one can recite slight fouling which can repeatedly occur during polymerisation and provoke periods of off specification materials, fouled lumps, ... ; hot spot phenomena related to points of higher than average temperature within the polymerisation zone ; static phenomena measured with static probes within the polymerisation zone were also part of the detailed analysis and study.

Surprisingly, the very simple process of the Applicants provides an industrial solution to all these problems, in particular to the fouling problems that could affect gas phase polymerisation of olefins with Ziegler-Natta type catalysts.

In accordance with the present invention, there has now been found a process for the gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst in the presence of a process aid additive wherein the additive comprises at least one of the components selected from :

- (1) a polysulphone copolymer,
- (2) a polymeric polyamine, and
- (3) an oil-soluble sulphonic acid.

Preferably, the process aid additive comprises at least two components selected from above components (1), (2) and (3). More preferably, the process aid additive comprises a mixture of (1), (2) and (3).

The process aid additive can be added at any location of the fluidised bed polymerisation system, e.g. in the reactor itself, below the fluidisation grid or above the grid in the fluidised bed, above the fluidised bed, in the powder disengagement zone of the reactor (also named velocity reduction zone), anywhere in the reaction loop or recycle line, in the fines recycle line (when a fines separator, preferably a cyclone, is used), etc... According to a preferred embodiment of the present invention, the process aid additive is directly added into the fines recycle line (when a fines separator, preferably a cyclone, is used), or directly into the polymerisation zone, more preferably directly into the fluidised bed, ideally into the lower part of the bed (below half bed height). For the purposes of the present invention and appended claims, the polymerisation zone means the reaction zone consisting of the fluidised bed itself, and the region above the fluidised bed which consists of the powder disengagement zone and/or the velocity reduction zone. According to another preferred embodiment of the present invention, the

process aid additive is added at at least two different locations of the fluidised bed polymerisation system. It is also particularly preferred according to the present invention that the process aid additive is not added in admixture with a catalyst component like the catalyst itself or the cocatalyst. According to another preferred embodiment, the process aid additive is added into the fluidised bed polymerisation system through the well known BP high productivity nozzles which protrude through the fluidisation grid directly into the fluidised bed (see e.g. W09428032, the content of which is incorporated hereby). It may also be preferred that the process aid additive is not added in admixture with a liquid comonomer used for the copolymerisation.

According to the present invention, the polysulphone copolymer component of the process aid additive (often designated as olefin-sulphur dioxide copolymer, olefin polysulphones, or poly(olefin sulphone)), is a polymer, preferably a linear polymer, wherein the structure is considered to be that of alternating copolymers of the olefins and sulphur dioxide, having a one-to-one molar ratio of the comonomers with the olefins in head to tail arrangement. Preferably, the polysulphone copolymer consists essentially of about 50 mole percent of units of sulphur dioxide, about 40 to 50 mole percent of units derived from one or more 1-alkenes each having from about 6 to 24 carbon atoms, and from about 0 to 10 mole percent of units derived from an olefinic compound having the formula $ACH=CHB$ where A is a group having the formula $-(C_xH_{2x})-COOH$ wherein x is from 0 to about 17, and B is hydrogen or carboxyl, with the proviso that when B is carboxyl, x is 0, and wherein A and B together can be a dicarboxylic anhydride group.

Preferably, the polysulphone copolymer employed in the present invention has a weight average molecular weight in the range 10,000 to 1,500,000, preferably in the range 50,000 to 900,000. The units derived from the one or more 1-alkenes are preferably derived from straight chain alkenes having 6-18 carbon atoms, for example 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-hexadecene and 1-octadecene. Examples of units derived from the one or more compounds having the formula $ACH=CHB$ are units derived from maleic acid, acrylic acid, 5-hexenoic acid. For further details of polysulphones particularly suitable for use in the present invention reference may be made to UK patent specifications 1,432,265, 1,432,266, and US patent specifications 3,811,848 and 3,917,466.

A preferred polysulphone copolymer is 1-decene polysulphone having an inherent

viscosity (measured as a 0.5 weight percent solution in toluene at 30°C) ranging from about 0.04 dl/g to 1.6 dl/g.

According to the present invention, the polymeric polyamine component of the process aid additive is preferably a polymeric polyamine having the general formula :



wherein R^1 is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms,

R^2 is an alkylene group of 2 to 6 carbon atoms,

R^3 is the group $-R^2-HNR^1$,

10 R is R^1 or an N-aliphatic hydrocarbyl alkylene group having the formula R^1NHR^2 ;

a , b and c are integers of 0-20 and x is 1 or 2; with the proviso that when R is R^1 then a is an integer of 2 to 20 and $b = c = 0$, and when R is R^1NHR^2 then a is 0 and $b+c$ is an integer of 2 to 20.

15 The polymeric polyamines which can be suitably employed in the process of the present invention are described in US patent 3,917,466, in particular at column 6 line 42 to column 9 line 29.

The polymeric polyamine may be prepared for example by heating an aliphatic primary monoamine or N-aliphatic hydrocarbyl alkylene diamine with epichlorohydrin in
20 the molar proportion of from 1:1 to 1:1.5 at a temperature of 50°C to 100°C in the presence of a solvent, eg a mixture of xylene and isopropanol, adding a strong base, eg sodium hydroxide and continuing the heating at 50 to 100°C for about 2 hours. The product containing the polymeric polyamine may then be separated by decanting and then flashing off the solvent.

25 The polymeric polyamine is preferably the product of reacting an N-aliphatic hydrocarbyl alkylene diamine or an aliphatic primary amine containing at least 8 carbon atoms and preferably at least 12 carbon atoms with epichlorohydrin. Examples of such aliphatic primary amines are those derived from tall oil, tallow, soy bean oil, coconut oil and cotton seed oil. The polymeric polyamine derived from the reaction of tallowamine
30 with epichlorohydrin is preferred. A method of preparing such a polyamine is disclosed in US patent specification 3,917,466, column 12, preparation B.1.0.

The above-described reactions of epichlorohydrin with amines to form polymeric

products are well known and find extensive use in epoxide resin technology.

A preferred polymeric polyamine is a 1:1.5 mole ratio reaction product of N-tallow-1,3-diaminopropane with epichlorohydrin. One such reaction product is "Polyflo 130" sold by Universal Oil Company.

5 According to the present invention, the oil-soluble sulphonic acid component of the process aid additive is preferably any oil-soluble sulphonic acid such as an alkane sulphonic acid or an alkylaryl sulphonic acid. A useful sulphonic acid is petroleum sulphonic acid resulting from treating oils with sulphuric acid.

10 Preferred oil-soluble sulphonic acids are dodecylbenzene sulphonic acid and dinonylnaphthyl sulphonic acid.

 In accordance with the present invention, the process aid additive preferably comprises 1 to 25 weight percent of the polysulphone copolymer, 1 to 25 weight percent of the polymeric polyamine, 1 to 25 weight percent of the oil-soluble sulphonic acid and 25 to 95 weight percent of a solvent. Neglecting the solvent, the process aid additive
15 preferably comprises about 5-70 weight percent polysulphone copolymer, 5-70 weight percent polymeric polyamine, and 5-70 weight percent oil-soluble sulphonic acid ; the total of course being 100 percent.

 Suitable solvents include aromatic, paraffin and cycloparaffin compounds.

20 The solvents are preferably selected from among benzene, toluene, xylene, cyclohexane, fuel oil, isobutane, kerosene and mixtures thereof for instance.

 According to a preferred embodiment of the present invention, the process aid additive is diluted in a conventional hydrocarbon diluent, which can be the same or different from the above solvent, preferably butane, pentane or hexane.

25 When a diluent is used, the process aid additive (including the solvent thereof) is preferably present in an amount comprised between 0.1 and 500 g per litre of diluent, preferably between 1 and 50 g per litre of diluent.

 According to a preferred embodiment of the present invention, the total weight of components (1), (2), (3), the solvent and the diluent represents essentially 100% of the weight of the process aid additive.

30 One useful composition, for example, consists of 13.3 weight percent 1:1 copolymer of 1-decene and sulphur dioxide having an inherent viscosity of 0.05 determined as above, 13.3 weight percent of "Polyflo 130" (1:1.5 mole ratio reaction

product of N-tallow-1,3-diaminopropane with epichlorohydrin), 7.4 weight percent of either dodecylbenzene sulphonic acid or dinonylnaphthyl sulphonic acid, and 66 weight percent of an aromatic solvent which is preferably toluene or kerosene.

Another useful composition, for example, consists of 2 to 7 weight percent 1:1
5 copolymer of 1-decene and sulphur dioxide having an inherent viscosity of 0.05 determined as above, 2 to 7 weight percent of "Polyflo 130" (1:1.5 mole ratio reaction product of N-tallow-1,3-diaminopropane with epichlorohydrin), 2 to 8 weight percent of either dodecylbenzene sulphonic acid or dinonylnaphthyl sulphonic acid, and 78 to 94 weight percent of an aromatic solvent which is preferably a mixture of 10 to 20 weight
10 percent toluene and 62 to 77 weight percent kerosene.

The additive composition of the present invention (including the solvent and diluent therefor) is preferably added to the reactor in an amount ranging from about 0.02 to about 50000 ppm, preferably from about 0.2 to about 10000 ppm, more preferably from about 2 to 1000 ppm, based on the weight of the olefin introduced into the reactor.

Based on the total weight of just the polysulphone polymer, polymeric amine and
15 oil-soluble sulphonic acid, the preferred concentration of the aid additive is from about 0.00001 to about 35, preferably from about 0.0001 to about 7.5, more preferably from about 0.006 to about 4 parts by weight per million parts by weight of the olefin introduced into the reactor.

20 The process aid additive can be added continuously or intermittently to the reactor. In the continuous gas phase polymerisation process according to the present invention, it is preferred to add continuously the additive to the reactor. Sufficient process aid additive is added to maintain its concentration at the desired level.

According to a preferred embodiment of the present invention, before the
25 Ziegler-Natta type catalyst is introduced into the reactor, the reactor is pre-loaded with the said process aid additive. This pre-load can be done before or after the introduction of the seed bed polymer into the reactor; however, it is preferred to perform the pre-load solely on the seed bed polymer.

For the pre-load, the additive composition of the present invention (including the
30 solvent and diluent therefor) is preferably added to the reactor in an amount ranging from about 0.02 to about 50000 ppm, preferably from about 0.2 to about 10000 ppm, more preferably from about 2 to 1000 ppm, based on the weight of the seed polymer bed.

Based on the total weight of just the polysulphone polymer, polymeric amine and oil-soluble sulphonic acid, the preferred concentration of the aid additive is from about 0.00001 to about 35, preferably from about 0.0001 to about 7.5, more preferably from about 0.006 to about 4 parts by weight per million parts by weight of the seed polymer bed.

According to a preferred embodiment of the present invention, the process aid additive is a material sold by Octel under the trade name STADIS, preferably STADIS 450, more preferably STADIS 425, said STADIS components being preferably added at a rate of 0.001 to 50 ppm by weight of the olefin introduced into the reactor and/or at a concentration of 0.01 to 10 ppm by weight of the seed polymer bed in case of pre-load.

In accordance with the present invention, there is also provided a process for preventing fouling during the gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst in the presence of a process aid additive characterised in that the additive comprises a mixture of

- (1) a polysulphone copolymer,
- (2) a polymeric polyamine, and
- (3) an oil-soluble sulphonic acid.

The process according to the present invention is suitable for the manufacture of polymers in a continuous gas fluidised bed process.

In an advantageous embodiment of this invention, the polymer is a polyolefin preferably copolymers of ethylene and/or propylene and/or butene. Preferred alpha-olefins used in combination with ethylene and/or propylene and/or butene in the process of the present invention are those having from 4 to 8 carbon atoms. However, small quantities of alpha olefins having more than 8 carbon atoms, for example 9 to 40 carbon atoms (e.g. a conjugated diene), can be employed if desired. Thus it is possible to produce copolymers of ethylene and/or propylene and/or butene with one or more C4-C8 alpha-olefins. The preferred alpha-olefins are but-1-ene, pent-1-ene, hex-1-ene, 4-methylpent-1-ene, oct-1-ene and butadiene. Examples of higher olefins that can be copolymerised with the primary ethylene and/or propylene monomer, or as partial replacement for the C4-C8 monomer are dec-1-ene and ethylidene norbornene.

According to a preferred embodiment, the process of the present invention preferably applies to the manufacture of polyolefins in the gas phase by the copolymerisation of

ethylene with but-1-ene and/or hex-1-ene and/or 4-methylpent-1-ene.

The process according to the present invention may be used to prepare a wide variety of polymer products for example linear low density polyethylene (LLDPE) based on copolymers of ethylene with but-1-ene, 4-methylpent-1-ene or hex-1-ene and high
5 density polyethylene (HDPE) which can be for example copolymers of ethylene with a small portion of higher alpha olefin, for example, but-1-ene, pent-1-ene, hex-1-ene or 4-methylpent-1-ene.

When liquid condenses out of the recycle gaseous stream, it can be a condensable monomer, e.g. but-1-ene, hex-1-ene, 4-methylpent-1-ene or octene used as
10 a comonomer, and/or an optional inert condensable liquid, e.g. inert hydrocarbon(s), such as C4-C8 alkane(s) or cycloalkane(s), particularly butane, pentane or hexane.

The process is particularly suitable for polymerising olefins at an absolute pressure of between 0.5 and 6 MPa and at a temperature of between 30°C and 130°C. For example for LLDPE production the temperature is suitably in the range 75-90°C and
15 for HDPE the temperature is typically 80-112°C depending on the activity of the catalyst used and the polymer properties desired.

The polymerisation is preferably carried out continuously in a vertical fluidised bed reactor according to techniques known in themselves and in equipment such as that described in European patent application EP-0 855 411, French Patent No. 2,207,145 or
20 French Patent No. 2,335,526. The process of the invention is particularly well suited to industrial-scale reactors of very large size.

In one embodiment the reactor used in the present invention is capable of producing greater than 300 Kg/hr to about 80,000 Kg/hr or higher of polymer, preferably greater than 10,000 Kg/hr.

25 The polymerisation reaction is carried out in the presence of a Ziegler-Natta type catalyst.

Examples of Ziegler-Natta type catalysts according to the present invention are typically those consisting of a solid catalyst essentially comprising a compound of a transition metal and of a cocatalyst comprising an organic compound of a metal (i.e. an
30 organometallic compound, for example an alkylaluminium compound). These high-activity Ziegler-Natta type catalyst systems have already been known for a number of years and are capable of producing large quantities of polymer in a relatively short time,

and thus make it possible to avoid a step of removing catalyst residues from the polymer. These high-activity catalyst systems generally comprise a solid catalyst consisting essentially of transition metal complexes, magnesium complexes and halogen containing complexes. Examples thereof can be found, e.g. in US4260709, EP0598094, EP0099774
5 and EP0175532. The process is also particularly suitable for use with Ziegler catalysts supported on silica, e.g. in WO9309147, WO9513873, WO9534380 and WO9905187. For the purpose of the present description and appended claims, Ziegler-Natta type catalysts specifically exclude the metallocene catalysts.

The catalyst can be used as it is or optionally in the form of a coated catalyst or
10 prepolymer containing, for example, from 10^{-5} to 3, preferably from 10^{-3} to 10^{-1} , millimoles of transition metal per gram of polymer. The process of the invention is particularly suited to the use of a non-prepolymerized catalyst, preferably to the direct introduction of a Ziegler-Natta supported catalyst, more preferably a silica supported titanium containing Ziegler-Natta catalyst.

15 The Ziegler-Natta type catalysts used in the present invention may be used together with a cocatalyst or activator, e.g. an organometallic compound of a metal from groups I to III of the Periodic Classification of the Elements, such as, for example, an organoaluminum compound.

The following non limiting examples illustrate the present invention.

20 Example 1

The catalyst is a silica supported catalyst which is the same as the one disclosed in example E1 of WO9513873, excepted that the silica support has been thermally treated at a temperature of 700°C (instead of 600°C) which gives a final OH content of 0.52.

25 The process is carried out in a fluidised bed gas phase polymerisation reactor consisting of a vertical cylinder of diameter 0.74 m and height 7 m and surmounted by a velocity reduction chamber. In its lower part, the reactor is equipped with a fluidisation grid and an external line for recycling gas, connecting the top of the velocity reduction chamber to the lower part of the reactor, situated under the fluidisation grid. The gas
30 recycling line is equipped with a compressor and with a heat transfer means. Opening into the gas recycling line there are, in particular, the feed lines for ethylene, 1-hexene and nitrogen which represent the main constituents of the gas reaction mixture passing

through the fluidised bed.

Above the fluidisation grid the reactor contains a fluidised bed consisting of a medium density polyethylene powder. The gas reaction mixture, which contains ethylene, 1-hexene, hydrogen, pentane and nitrogen passes through the fluidised bed at a pressure
5 of 2 MPa, at 93 °C and with an upward fluidisation velocity of 0.55 m/s.

The gas phase is composed with 0.8 MPa of ethylene, and molar ratio of hydrogen to ethylene at 0.18 ; hexene-1 to ethylene partial pressure at 0.08.

The catalyst is introduced into the reactor, at a rate of 20g/h ; simultaneously a solution of triethylaluminium diluted in pentane at a concentration of 0.5 moles of
10 TEA/litre of pentane, is injected at 0.75 litre/h.

No process aid additive is injected.

Since the start-up and until when the production rate reaches 180 kg/h, hot spots started rapidly to appear on the internal penetrating temperature probes, as well as on the skin temperature probes located in the 0.8 to 1.2 m (above the fluidisation grid) zone of
15 the reactor.

It was then decided to introduce STADIS 425 into the reactor. It is previously diluted in pentane in a ratio of 7 g of STADIS 425 per litre of pentane.

The solution of STADIS 425 was injected into the polymerisation reactor at 1 meter above the grid at flow rate of 0.2 l of diluted Stadis per hour. Within 5 minutes
20 all the temperature probes became much more stable. No agglomerates were produced, while production rate could then be safely increased to 230kg/h.

A flowability measurement made on the polyethylene before and after the addition of STADIS revealed a much better value obtained by applying the present invention. The present invention consequently also relates to a process for improving the
25 polymer flowability and the fluidisation characteristics during the gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta catalyst.

At the end of the run, the reactor was opened/inspected and revealed no indication of fouling, i.e. the reactor wall (the cylindrical section as well as the bulb) was perfectly clean.

30 Example 2

The process is carried out in the same reactor as in example 1 and with the same catalyst system.

Above the fluidisation grid the reactor contains a fluidised bed consisting of a medium density polyethylene powder. The gas reaction mixture, which contains ethylene, 1-hexene, hydrogen, pentane and nitrogen passes through the fluidised bed at a pressure of 2 MPa, at 102 °C and with an upward fluidisation velocity of 0.55 m/s.

5 The gas phase is composed with 0.8 MPa of ethylene, and molar ratio of hydrogen to ethylene at 0.13 ; hexene-1 to ethylene partial pressure at 0.08.

The catalyst is introduced into the reactor, at a rate of 20g/h ; simultaneously a solution of triethylaluminium diluted in pentane at a concentration of 0.5 moles of TEA/litre of pentane, is injected at 0.75 litre/h.

10 No process aid additive is injected.

Since the start-up and until when the production rate reaches 200 kg/h, hot spots started rapidly to appear on the internal penetrating temperature probes, as well as on the skin temperature probes located in the 0.8 to 1.2 m (above the fluidisation grid) zone of the reactor.

15 It was then decided to introduce STADIS 425 into the reactor. It is previously diluted in pentane in a ratio of 1 g of STADIS 425 per litre of pentane.

The solution of STADIS 425 was injected into the polymerisation reactor at 1 meter above the grid at flow rate of 0.2 l of diluted Stadis per hour. Within 5 minutes all the temperature probes became much more stable. No agglomerates were produced,
20 while production rate could then be safely increased to 230kg/h.

At the end of the run, the reactor was opened/inspected and revealed no indication of fouling, i.e. the reactor wall (the cylindrical section as well as the bulb) was perfectly clean.

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Claims

1. Process for the continuous gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst in the presence of a process aid additive wherein the additive comprises at least one of the components selected from :
 - (1) a polysulphone copolymer,
 - 5 (2) a polymeric polyamine, and
 - (3) an oil-soluble sulphonic acid.
2. Process according to claim 1 wherein the process aid additive is directly added into the polymerisation zone.
3. Process according to claim 2 wherein the process aid additive is directly added
10 into the fluidised bed polymerisation reaction zone.
4. Process according to any of the preceding claims wherein the process aid additive is not added in admixture with the catalyst or the cocatalyst.
5. Process according to any of the preceding claims wherein the process aid additive comprises at least two components selected from above components (1), (2) and (3).
- 15 6. Process according to claim 5 wherein the process aid additive comprises a mixture of (1), (2) and (3).
7. Process according to any of the preceding claims wherein the process aid additive comprises about 5-70 weight percent polysulphone copolymer, 5-70 weight percent polymeric polyamine, and 5-70 weight percent oil-soluble sulphonic acid.
- 20 8. Process according to any of the preceding claims wherein the process aid additive represents from about 0.00001 to about 35, preferably from about 0.0001 to about 7.5 , more preferably from about 0.006 to about 4 parts by weight per million parts by weight

of the olefin introduced into the reactor.

9. Process according to any of the preceding claims wherein the reactor is pre-loaded with the said process aid additive before the Ziegler-Natta type catalyst is introduced into the reactor.

5 10. Process according to claim 9 wherein the pre-load is performed solely on the seed bed polymer.

11. Process according to any of the preceding claims wherein the process aid additive is selected from STADIS 450 and STADIS 425.

10 12. Process according to any of the preceding claims wherein the sole or main olefin is either ethylene or propylene, and the optional comonomer is selected from but-1-ene, pent-1-ene, hex-1-ene, 4-methylpent-1-ene and oct-1-ene.

13. Process according to claim 12 wherein the main olefin is ethylene and the optional comonomer is selected from but-1-ene, hex-1-ene or 4-methylpent-1-ene.

14. Ethylene (co)polymer obtainable by the process of any of the preceding claims.

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